The kinetics of the gas-phase reactions of selected monoterpenes and cyclo-alkenes with ozone and the NO3 radical

Atmospheric Environment 70 (2013) 227–235

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

The kinetics of the gas-phase reactions of selected monoterpenes and cyclo-alkenes with ozone and the NO_3 radical

D.J. Stewart*, S.H. Almabrok, J.P. Lockhart, O.M. Mohamed, D.R. Nutt, C. Pfrang, G. Marston

Department of Chemistry, University of Reading, Whiteknights, PO Box 224, Reading RG6 6AD, UK

HIGHLIGHTS

- Measurements of rate constants for the reactions of O_3 and NO_3 with terpenes and cyclo-alkenes are presented.
- The effect of structure on the observed kinetics is discussed.
- Measured values are evaluated along with literature data to give recommended rate constants.
- Atmospheric lifetimes and presented in light of this data.

ARTICLE INFO

Article history:
Received 25 September 2012
Received in revised form
14 January 2013
Accepted 18 January 2013

Keywords:
Kinetics
Ozone
Nitrate radical
Terpenes
Alkenes

ABSTRACT

The relative rate method has been used to measure the room-temperature rate constants for the gas-phase reactions of ozone and NO_3 with selected monoterpenes and cyclo-alkenes with structural similarities to monoterpenes. Measurements were carried out at 298 ± 2 K and 760 ± 10 Torr. The following rate constants (in units of 10^{-18} cm^3 $molecule^{-1}$ s^{-1}) were obtained for the reaction with ozone: methyl cyclohexene (132 ± 17), terpinolene (1290 ± 360), ethylidene cyclohexane (223 ± 57), norbornene (860 ± 240), *t*-butyl isopropylidene cyclohexane (1500 ± 460), cyclopentene (543 ± 94), cyclohexene (81 ± 18), cyclooctene (451 ± 66), dicyclopentadiene (1460 ± 170) and α-pinene (107 ± 13). For the reaction with NO_3 the rate constants obtained (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) were: methyl cyclohexene (7.92 ± 0.95), terpinolene (47.9 ± 4.0), ethylidene cyclohexane (4.30 ± 0.24), norbornene (0.266 ± 0.029), cyclohexene (0.540 ± 0.017), cyclooctene (0.513 ± 0.029), dicyclopentadiene (1.20 ± 0.10) and α-pinene (5.17 ± 0.62). Errors are quoted as the root mean square of the statistical error (95% confidence) and the quoted error in the rate constant for the reference compound. Combining these results with previous studies, new recommendations for the rate constants are presented. Molecular orbital energies were calculated for each alkene and the kinetic data are discussed in terms of the deviation from the structure–activity relationship obtained from the rate constants for a series of simple alkenes. Lifetimes with respect to key initiators of atmospheric oxidation have been calculated suggesting that the studied reactions play dominant roles in the night-time removal of these compounds from the atmosphere.

1. Introduction

Oxidation of organic compounds in the troposphere is primarily initiated by OH radicals, ozone or the nitrate radical, the dominant oxidant being determined by the relative concentrations of the oxidants and the rate constants for the reactions of the individual oxidised compounds with these species. The most important oxidant during the day is the OH radical, with NO_3-initiated oxidation dominating at night; this situation arises because the major atmospheric source of OH is photochemical and the fact that during the day NO_3 is rapidly photolysed with a lifetime of ~5 s, and in the presence of NO the lifetime is significantly shorter (Finlayson-Pitts and Pitts, 2000). The concentration of ozone is not dependent on purely photochemical processes and is an important oxidant both during the day and at night.

The oxidation of volatile organic compounds (of which alkenes form a significant component) in the atmosphere is important for a number of reasons. Oxidation products, both closed shell (carbonyl species) and radicals (OH, HO_2 and RO_2) have a major importance in the chemistry of the troposphere (Johnson and

* Corresponding author. Present address: Department of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK. Tel.: +44 (0)1173317417; fax: +44 (0) 1179277985.
E-mail address: dj.stewart@bristol.ac.uk (D.J. Stewart).

1352-2310/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.atmosenv.2013.01.036

Marston, 2008). Modelling studies have shown that the reaction of ozone with alkenes could be the dominant source of HO_x in polluted urban environments as well as being a significant contributor in less polluted rural locations (Paulson and Orlando, 1996). The oxidation of volatile organic compounds (VOCs) can also contribute significantly to the nucleation and production of aerosol particles in the atmosphere (Went, 1960; Marti et al., 1997), which has a significant effect on air quality, global climate (Twomey et al., 1984; Charlson et al., 1992), cloud formation (Novakov and Penner, 1993) and also has important impacts on visibility and human health (Donaldson et al., 1998; Gaschen et al., 2010).

The oxidation of alkenes by the nitrate radical is known to produce nitrated compounds (Barnes et al., 1990; Berndt and Böge, 1997; Perraud et al., 2010; Harrison and Ham, 2009). The oxidation of large alkenes produces organic alkyl nitrates which can act as temporary reservoirs of odd nitrogen in the atmosphere. These compounds are not photodissociated in the troposphere but have the potential to be photolysed in the stratosphere (Aschmann et al., 2011 and references therein, Suarez-Bertoa et al., 2012).

Understanding the kinetics of these reactions is therefore of crucial importance for understanding tropospheric chemistry. At present the level of detail with regard to these processes in tropospheric models is lacking with "average" representative rate constants being used for whole classes of compounds. The errors associated with this approach are obviously potentially very large and so kinetic data on a wider range of such compounds is required to improve the representation of these processes in tropospheric chemistry models.

In this paper we report results of a kinetic study of the reactions of a range of selected monoterpenes and structurally similar cycloalkenes to attempt to elucidate the effect of structure on the reactivity of these compounds with ozone and the NO_3 radical and interpret the results by use of structure activity relationships. One way of accomplishing this is by investigating the energy of the highest occupied molecular orbital (HOMO), corresponding to the double-bond π orbital which is the reactive site for oxidation of alkenes by ozone and NO_3 (Johnson et al., 2000; Johnson and Marston, 2008). HOMO energies were obtained for a number of molecules in their optimised geometries at the HF/6-31G and MP2/6-311++G** levels using Gaussian03 (Frisch et al., 2003). The two values were found to be of comparable accuracy, so the less-expensive HF/6-31G level was adopted for the rest of the calculations. A range of starting geometries were used to ensure that the global minimum was found in the geometry optimisation, with only the lowest energy structure being retained for the analysis.

2. Materials and methods

The experimental apparatus employed for this study (described in detail in Ma and Marston (2009)) consisted of a static reaction chamber coupled to gas chromatography flame ionisation detector (GC-FID). Experiments were carried out at 298 ± 2 K. A mixture of the alkene under study and a reference compound for which the rate constant is known were prepared in an 80 L collapsible Teflon chamber using dry synthetic air (BOC) as a diluent gas (in the ozone experiments cyclohexane was also added at a concentration sufficient to scavenge ≥95% of any OH radicals formed). Typical initial concentrations employed were ~10 ppmv of each alkene. Experiments were carried out by admitting a known concentration of ozone (or N_2O_5) into a 1 L borosilicate glass bulb at a total pressure of *ca.* 7 Torr and adding the hydrocarbon mixture from the bag until atmospheric pressure (760 ± 10 Torr) was reached this took 1–2 s. Ozone was generated as a mixture in O_2 by passing pure oxygen through a Fischer ozone generator, its purity being measured spectroscopically by absorption at λ = 254 nm N_2O_5 was synthesised prior to use by the reaction of ozone and NO and trapped until needed; the amount of NO_3 in the bulb was estimated from the pressure of N_2O_5 admitted to the system and the equilibrium constant for dissociation (Osborne et al., 2000). After a reaction time of 10 min the contents of the bulb were separated and detected by gas chromatography (two instruments were used, a Thermo Finnegan TraceGC, employing a 30 m × 0.25 mm i.d. DB-5 column and a Varian CP3800 GC employing a 30 m × 0.53 mm i.d. fused silica WCOT column) with flame ionisation detection. This procedure was repeated for a minimum of six different ozone/NO_3 concentrations (1–6 ppmv) during each study except in the case of *t*-butyl isopropylidene cyclohexane where the small amount available limited the experiment to four different concentrations. All gaseous reagents used were provided by BOC Industrial Gases Ltd. and reported to be ≥95% in purity; these were used without further processing. All other reagents used were in most cases analytical-reagent grade (with the exception of terpinolene ~90% and *t*-butyl isopropylidene cyclohexane which came from the Aldrich rare chemicals library and had no stated purity) and underwent a freeze–pump–thaw cycle before being used.

Experimental results were interpreted using the relative rate expression (Shu and Atkinson, 1994), with a plot of $\ln([\text{alkene}]_i/[\text{alkene}])$ *vs.* $\ln([\text{reference}]_i/[\text{reference}])$ giving the relative rate constant according to Eq. (1)

$$\ln\left(\frac{[\text{alkene}]_i}{[\text{alkene}]}\right) = \frac{k_{\text{alkene}}}{k_{\text{reference}}} \times \ln\left(\frac{[\text{reference}]_i}{[\text{reference}]}\right) \quad (1)$$

(k_{alkene} and $k_{\text{reference}}$ are the rate constants for the reactions of the alkene being studied and the chosen reference compound with the oxidant used, $[\text{alkene}]_i$ and $[\text{reference}]_i$ are the initial concentrations of the alkene and reference with no oxidant present (measured from the bag before the ozone is added) and [alkene] and [reference] are the concentrations of these species after reaction). Relative rate constants were obtained from the slopes of the linear least-squares best fits to the data; best-fit lines were not forced through the origin.

3. Results and discussion

3.1. Experimental kinetics

Table 1 lists the reference rate constants used in this work. Fig. 1 illustrates the relative-rate plots obtained for the ozone reactions studied, and Fig. 2 illustrates the relative rate plots for the NO_3 reactions. The plots are linear, and for NO_3 reactions, all pass

Table 1
Reference rate constants.

Compound	k/cm^3 molecule^{-1} s^{-1}	Reference	Comments
β-Pinene + O_3	$(23.5 \pm 2.7) \times 10^{-18}$	Johnson et al., 2000	Relative rate with methylpropene as reference (relative rate = 2.08)
Limonene + O_3	$(201 \pm 6) \times 10^{-18}$	Shu and Atkinson, 1994	Relative rate with Z-2-butene as reference (relative rate = 1.65)
Cycloheptene + O_3	$(236 \pm 21) \times 10^{-18}$	Treacy et al., 1997	Absolute, measured directly
Limonene + NO_3	$(9.4 \pm 0.9) \times 10^{-12}$	Martinez et al., 1999a	Absolute, measured directly
Cycloheptene + NO_3	$(0.54 \pm 0.02) \times 10^{-12}$	Kind et al., 1998	Relative rate with E-2-butene as reference (relative rate = 1.29)

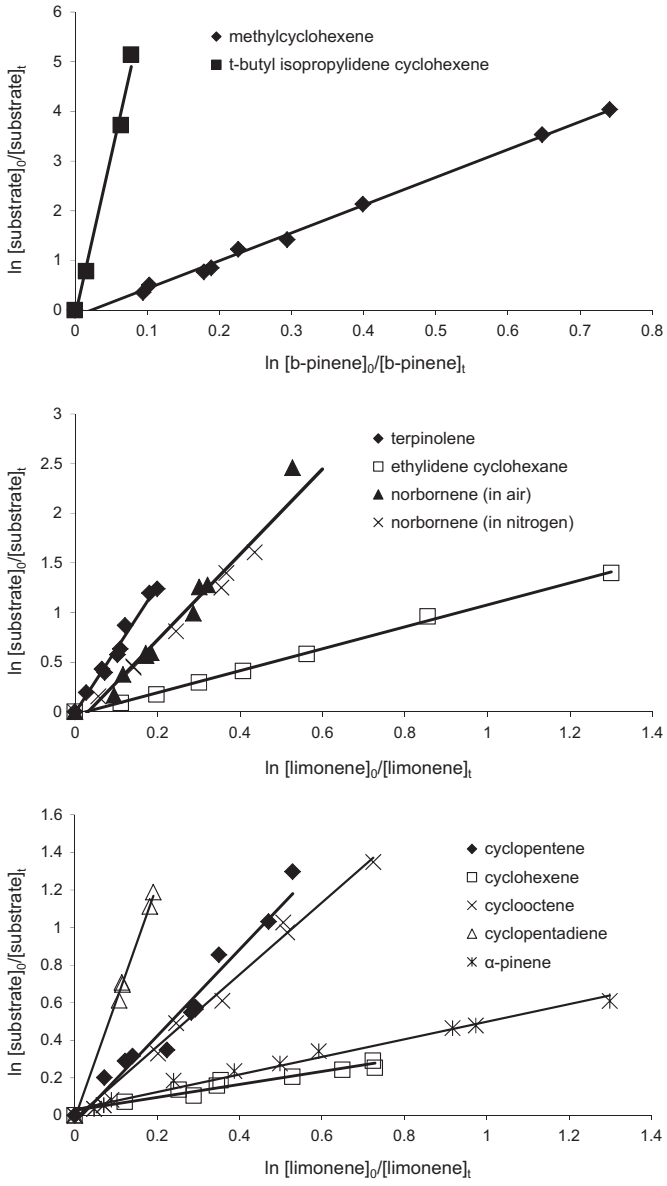


Fig. 1. Relative rate plots for the ozone reactions.

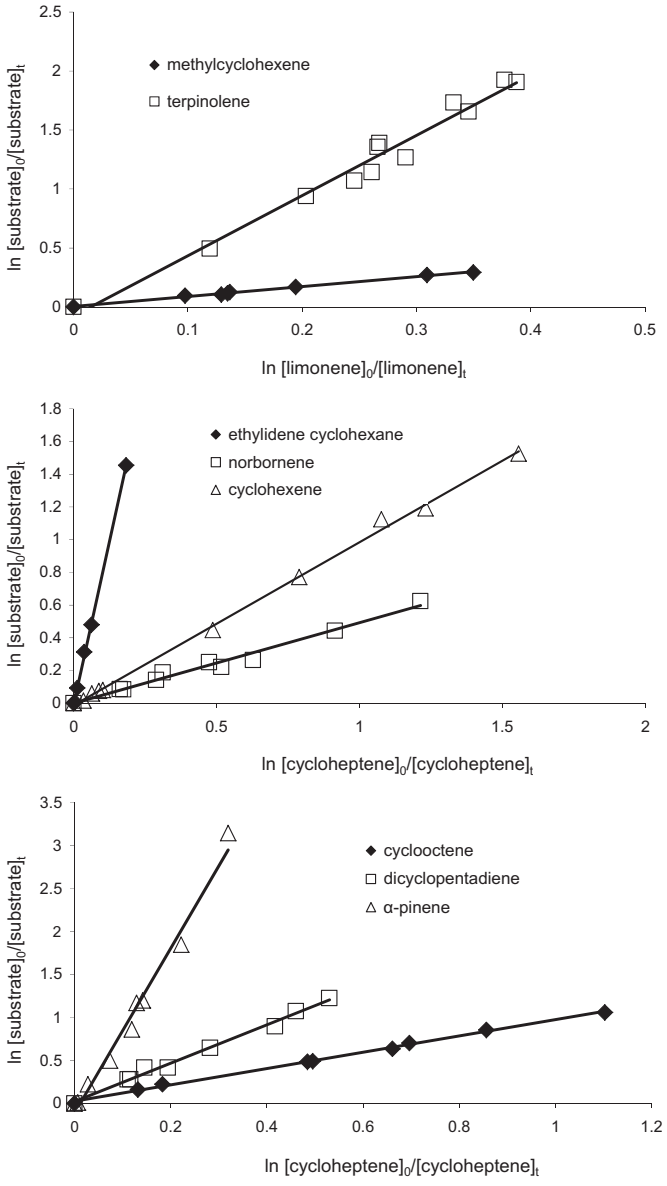


Fig. 2. Relative rate plots for NO_3 reactions.

through the origin within error at 95% confidence; for ozone reactions, two plots need to be examined further. For the reaction of ozone with norbornene in air, the intercept of the best-fit line does not quite go through the origin. Removing the single point where the consumption of reactant (91%) is greatest (and hence the error in the measurement is greatest) brings the intercept through the origin within error, and when all of the data are combined with the data obtained in nitrogen, the best-fit line goes through the origin within error. For the reaction of ozone with α-pinene, we obtain a positive intercept outside the error, but note that the rate constant obtained from this plot agrees with previous studies; it is not clear why this plot shows a positive intercept.

The relative rate constants and hence rate constants obtained in this study are summarised in Table 2 for the reactions with ozone and Table 3 for the reactions with NO_3, along with previously published values (where available). Errors quoted for the relative rate constants are the statistical errors at 95% confidence levels calculated from the least squares analyses. Errors quoted for the rate constants also include the quoted error in the rate constant for the reference compounds, and are calculated as the root mean square of the two errors. It is expected that the error in the rate constant for the reference compound will be the major source of systematic error in the rate constant. As can be seen from the tables, the rate constants determined in this study are – within quoted errors – in good agreement with previously published values. The main exception of norbornene with ozone. The reason for this difference is not clear and experiments carried out using N_2 as the diluent gas to replicate the conditions from the previously published study resulted in a rate constant that agreed with that obtained in air to within 10%. For the reaction of NO_3 with methyl cyclohexene our value of $(7.91 \pm 0.76) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is in agreement within error with the value of $(9.7 \pm 0.1.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} reported by Martinez et al., but is significantly lower than the value of (15 ± 5) cm^3 molecule^{-1} s^{-1} reported by Ljungstrom et al. Our work therefore strongly supports the lower value of Martinez et al.; our rate constants for the reactions of NO_3 with terpinolene and cyclohexene are also in good agreement with values reported by this group.

In Tables 2 and 3, we also include recommended values for the rate constants as weighted averages of our values and those from previous studies, with the errors calculated as the sum of the squares of the individual errors divided by the square root of the number of measurements. For most of the reactions, the agreement is good within quoted errors, and this approach seems reasonable. For reasons explained in the previous paragraph, we exclude from the calculations the value reported by Ljungstrom et al. for the reaction of NO_3 with methyl cyclohexene. For the reaction of ozone with norbornene, our measurement and the only other measurement disagree significantly and so we provide a range of possible values for the rate constant.

3.2. Structure activity relationship

Table 4 lists the energies of the highest occupied molecular orbital (HOMO) of the alkenes calculated using Gaussian03 at the HF/6-31G level of theory, and $-\log k$ for each reaction as well as calculated asymmetry factors for the molecular orbitals on the carbon atoms in the double bond. The asymmetry factors were

Table 2
Measured rate constants for reaction with ozone.

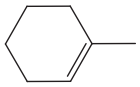
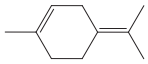
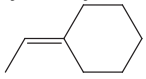
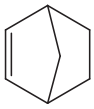
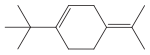
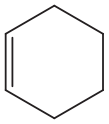
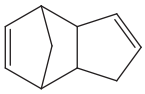
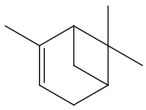
Alkene	Reference[a]	k (this work)[b,c]	k (literature)[b]	k (recommended)[a,d]
Methyl cyclohexene 	β-Pinene Relative rate = 5.60 ± 0.34	132 ± 17	146 ± 10 (Cusick and Atkinson, 2005) relative rate with Z-but-2-ene reference (relative rate = 1.20) 153 ± 23 (Cusick and Atkinson, 2005) relative rate with 2-methylbut-2-ene as reference (relative rate = 0.39)	143 ± 17
Terpinolene 	Limonene Relative rate = 6.41 ± 0.80	1290 ± 360	1880 ± 670 (Shu and Atkinson, 1994) relative rate with 2,3-dimethylbut-2-ene as reference (relative rate = 1.68) 1600 ± 400 (Witter et al., 2002) relative rate with 2,3-dimethylbut-2-ene as reference	1540 ± 500
Ethylidene cyclohexane 	Limonene Relative rate = 1.11 ± 0.05	223 ± 57	N/A	223 ± 57
Norbornene 	Limonene Air diluent Relative rate = 4.18 ± 0.70	840 ± 260		
	N_2 diluent Relative rate = 3.77 ± 0.29	760 ± 200		
	All data Relative rate = 4.30 ± 0.43	860 ± 240	1700 ± 150 (Greene and Atkinson, 1994) relative rate with propene as reference (relative rate = 170)	580 – 1850
t-Butyl isopropylidene cyclohexane 	β-Pinene Relative rate = 64.4 ± 18	1500 ± 460	N/A	1500 ± 460
Cyclopentene 	c-Heptene Relative rate = 2.30 ± 0.34	543 ± 94	654 ± 47 (Greene and Atkinson, 1992) relative rate with propene as reference (relative rate = 64.90) 624 ± 38 (Nolting et al., 1988) Relative rate with Z-but-2-ene as reference	620 ± 65
Cyclohexene 	c-Heptene Relative rate = 0.345 ± 0.07	81 ± 18	84.5 ± 8.5 (Grosjean and Grosjean, 1995) Absolute value measured directly 74.6 ± 5.2 (Greene and Atkinson, 1992) relative rate with propene reference (relative rate = 7.38) 78 ± 4.7 (Nolting et al., 1988) Relative rate with Z-2-butene as reference	78 ± 11
Cyclooctene 	c-Heptene Relative rate = 1.91 ± 0.22	451 ± 66	386 ± 23 (Cusick and Atkinson, 2005) relative rate with 2-methyl-2-butene as reference (relative rate = 0.98)	403 ± 49

Table 2 (*continued*)

Alkene	Reference[a]	*k* (this work)[b,c]	*k* (literature)[b]	*k* (recommended)[a,d]
Dicyclo-pentadiene 	c-Heptene Relative rate = 6.20 ± 0.45	1460 ± 170	N/A	1460 ± 170
α-Pinene 	c-Heptene Relative rate = 0.453 ± 0.036	107 ± 13	110 ± 20 (Witter et al., 2002) relative rate with 2-methyl-2-butene as reference (relative rate = 0.27) 82 ± 12 (Nolting et al., 1988) relative rate with Z-2-butene as reference (relative rate = 0.66)	98 ± 15

[a] Errors for relative rate values are statistical at 95% confidence.
[b] Units for rate constants are 10^{-18} cm^3 molecule^{-1} s^{-1}.
[c] Errors for rate constants obtained in this work include statistical error (95% confidence) and the error in the rate constant for the reference compound.
[d] Errors for recommended rate constants combine the errors from all measurements.

determined as $(c_1/c_2)^2$, where c_1 and c_2 are the molecular orbital coefficients for the HOMO obtained at the optimised geometry, with $c_1 \geq c_2$. The orbital coefficients represent the contribution of individual atomic orbitals to the molecular orbital of interest. For the HOMO, which corresponds to the C–C double bond, these are carbon p-π orbitals which are easily identifiable. Given the valence double-zeta basis set used, there are two pairs of orbital coefficients ('2P' and '3P') which can be considered, which yielded similar asymmetry factors; the values listed in Table 4 were derived from the '2P' coefficients. Also included in the table are the data for the simple alkenes ethene, propene, 2,3-dimethyl-2-butene, 2-methyl-2-butene, Z-2-butene and E-2-butene which have been used to provide the structure activity relationship with which to compare our kinetic data (Johnson et al., 2000).

The data sets obtained and summarised in Table 4 are plotted in Fig. 3 (ozone reactions) and Fig. 4 (NO_3 reactions) as the negative logarithm of the rate constant *vs*. the calculated HOMO energies for each alkene species. The trend line shown is that for the simple alkenes (ethene to butenes in Table 4) so that the data obtained in this study can be compared to the trend in reactivity of these compounds. The dependence of $-\log k$ on E(HOMO) for the simple alkenes can be rationalised in terms of the influence of E(HOMO) on the activation barrier, as discussed by Aird et al. (1992). What is immediately apparent from these data is the larger amount of scatter in the data for ozone reactions compared to those for reaction with NO_3. This is consistent with the earlier research (e.g. King et al., 1999; Johnson et al., 2000; Pfrang et al., 2006a, 2006b, 2007, 2008). This has been attributed to the fact that NO_3 can be thought of as a "point" reactant that will add to one or the other end of the double bond, whereas for ozone the reaction is a concerted cycloaddition that leads to a primary ozonide as the initial product. The spatial requirements for this cyclic process will be considerably stricter than for the formation of a single new bond at one end of the double bond. As will be seen later this is one of the factors by which the kinetics of the alkenes studied in this work can be rationalised.

3.3. Ozone reactions

As can be seen from Fig. 3, most of the compounds with exocyclic double bonds – (terpinolene, and *t*-butyl isopropylidene cyclohexane) lie close to the regression line of simple alkenes indicating that steric effects play only a minor role in the kinetics of their ozonolysis reactions. The exception to this is ethylidene

Table 3
Measured rate constants for reaction with NO_3.

Alkene	Reference[a]	*k* (this work)[b,c]	*k* (literature)[b]	*k* (recommended)[b,d]
Methyl cyclohexene	Limonene Relative rate = 0.84 ± 0.06	7.92 ± 0.95	15 ± 5 (Ljungstrom et al., 1993) 9.7 ± 1.6 (Martinez et al., 1999b) both fast flow discharge measurements	8.60 ± 1.30
Terpinolene	Limonene Relative rate = 5.10 ± 0.43	47.90 ± 4.00	52.0 ± 9.0 (Martinez et al., 1999a) absolute measurement measured directly	49.60 ± 7.70
Ethylidene cyclohexane	Cycloheptene Relative rate = 7.97 ± 0.33	4.30 ± 0.24	N/A	4.30 ± 0.24
Norbornene	Cycloheptene Relative rate = 0.493 ± 0.054	0.27 ± 0.03	0.27 ± 0.02 (Atkinson, 1991) review	0.27 ± 0.03
Cyclohexene	Cycloheptene Relative rate = 1.00 ± 0.03	0.54 ± 0.02	0.64 ± 0.08 (Martinez et al., 1999b) absolute value measured directly 0.49 ± 0.05 (Kind et al., 1998) relative rate with E-2-butene as reference (relative rate = 1.26)	0.54 ± 0.06
Cyclooctene	Cycloheptene Relative rate = 0.949 ± 0.049	0.51 ± 0.03	N/A	0.51 ± 0.03
Dicyclo-pentadiene	Cycloheptene Relative rate = 2.23 ± 0.018	1.20 ± 0.10	N/A	1.20 ± 0.10
α-Pinene	Cycloheptene Relative rate = 9.58 ± 1.10	5.17 ± 0.62	5.83 ± 0.58 (Kind et al., 1998) relative rate with 2-methyl-2-butene as reference (relative rate = 0.62) 6.16 ± 1.8 (Atkinson, 1991) review	5.60 ± 1.15

[a] Errors for relative rate values are statistical at 95% confidence.
[b] Units for rate constants are 10^{-12} cm^3 molecule^{-1} s^{-1}.
[c] Errors for rate constants obtained in this work include statistical error (95% confidence) and the error in the rate constant for the reference compound.
[d] Errors for recommended rate constants combine the errors from all measurements.

Table 4
Calculated HF/6-31G molecular orbital energies, asymmetry factor and −log *k* for each alkene.

Compound	−log (k/cm^3 molecule^{-1} s^{-1}) O_3	−log (k/cm^3 molecule^{-1} s^{-1}) NO_3	*E*(HOMO)/eV	Asymmetry factor
Methyl cyclohexene	15.88	11.10	8.867	1.11
Terpinolene	14.90	10.33	8.546	1.031
Ethylidene cyclohexane	15.65	11.36	8.823	1.141
Norbornene	15.02	12.57	9.079	1.000
t-Butyl isopropylidene cyclohexane	14.82	N/A	8.543	1.039
Cyclopentene	15.26	12.15	9.149	1.000
Cyclohexene	16.09	12.27	9.185	1.000
Cyclooctene	15.34	12.29	9.138	1.004
Dicyclo-pentadiene	14.84	12.62	9.024 endo 8.817 exo	1.148
α-Pinene	16.02	11.28	8.648	1.201
Ethene	17.80	15.60	10.194	1.000
Propene	17.00	14.02	9.687	1.161
2,3-Dimethyl-2-butene	14.96	10.24	8.626	1.000
2-Methyl-2-butene	15.39	11.03	8.908	1.100
Z-2-butene	15.89	12.46	9.226	1.000
E-2-butene	15.72	12.41	9.227	1.000

cyclohexane which reacts more slowly than would be expected. For the compounds with endocyclic double bonds, however, the data are significantly different from those which would be expected on the basis of orbital effects alone with cyclohexene, methyl cyclohexene and α-pinene reacting increasingly more slowly than would be expected and the cyclo-alkenes (except cyclohexene), dicyclopentadiene and norbornene reacting more quickly than would be expected from the simple alkene regression. These anomalous compounds will now be discussed.

It is worth first considering the effect of the asymmetry factors listed in Table 4. Johnson et al. (2000) identified a correlation between the deviation from expected rate constant and the asymmetry factor. Broadly speaking, this work indicated that an asymmetry factor of 1.2 caused a reduction in rate constant of about a factor of three compared to the rate constant for the reaction of ozone with a compound with the same value of *E*(HOMO) but no asymmetry. On this basis, the rate constant for the reaction of ozone with α-pinene may be slower than expected by a factor of three, but Fig. 3 indicates that it is slower than expected by a factor of ten. Clearly, other factors are involved, and Johnson et al. noted that asymmetry across the C—C double bond was not the only cause of unusual rate constants. Inspection of Table 4 shows that the asymmetry factors for the other compounds considered here are smaller than for α-pinene and we do not expect them to have a significant impact on the observed rate constants. As stated earlier, cyclohexene and methyl cyclohexene react more slowly with ozone than predictions considering frontier orbital energy alone would suggest. However, the analogous simple alkenes, 2-methyl-2-butene and E-2-butene, do fit the simple alkene regression line. The double bond of the simple alkenes have a conventional planar structure, while the double bond of these cyclic compounds is subject to the conformational constraints of a 6-carbon ring system containing two sp^2 hybridised carbons. When a single double bond

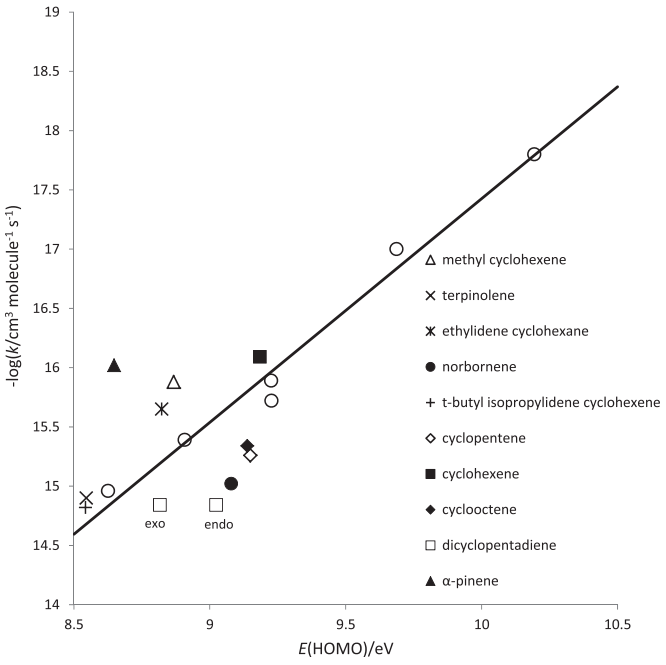


Fig. 3. Plot of −log *k* *vs.* *E*(HOMO) for ozone reactions. Best fit line is for simple alkenes (open circles).

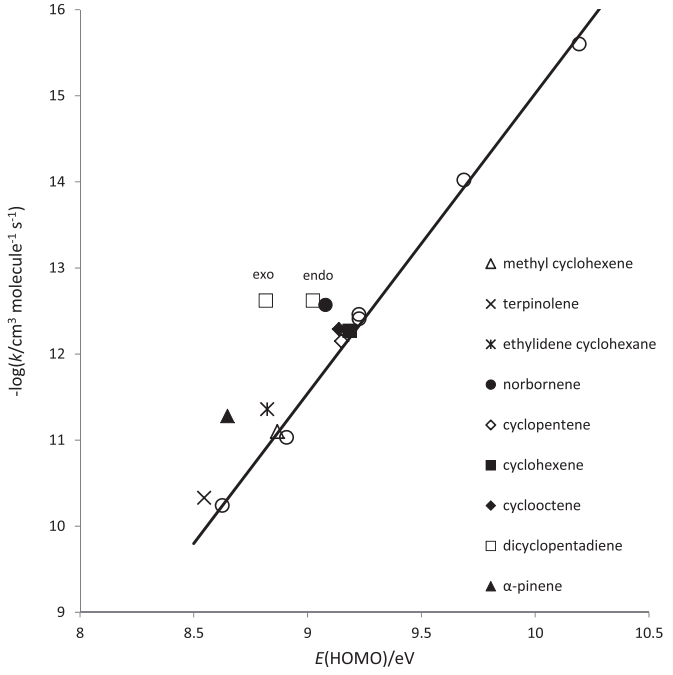


Fig. 4. Plot of −log *k* *vs.* *E*(HOMO) for NO_3 reactions. Best fit line is for simple alkenes (open circles).

is introduced to cyclohexane, there is an induced flattening of the chair conformation, to leave cyclohexene with a half-chair conformation (Clayden et al., 2001) which could inhibit reaction with ozone. In methyl cyclohexene and α-pinene the methyl substituent of one of the sp^2 carbons may induce a further steric hindrance or alter the orientation of the double bond frontier orbitals, such that overlap with the ozone orbitals is compromised. The much slower rate of α-pinene can be rationalised in the same way with the further reduction in rate being attributed to the steric effect of the bridgehead carbon out of the plane of the six membered ring.

Norbornene, dicyclopentadiene and the cyclo-alkenes (except cyclohexene) all react more quickly than would be expected from the simple alkene regression line. To understand the accelerated rate with which norbornene reacts with ozone, consideration must be given to the strained nature of the norbornene structure (compare e.g. Pfrang et al., 2005: surprisingly large differences in the reactivity of *Z*–*E* isomeric alkenes have been rationalised in terms of a combination of steric and inductive effects). The carbon skeleton of norbornane comprises a cyclohexane ring, bridged by a methylene group in the 1,4 position, while the norbornene structure carries a double bond between carbons 2 and 3.

The conformations of cyclohexane have been well documented, and heat of combustion data show the chair conformation of cyclohexane to be virtually strain free. The tendency for sp^3 hybrid carbons to form bond angles close to 109.5° is satisfied and all of the carbon–hydrogen bonds are fully staggered, such that there is no torsional strain to compromise the molecular energy (Clayden et al., 2001). The bridging methylene group of norbornane has to be diaxial to span the ring, and as a result the cyclohexane component of the bicyclic structure is locked into the higher-energy boat conformation. Consequently all of the carbon–hydrogen bonds, except those of the bridging group, eclipse those of neighbouring carbons, this structure is further strained by the C=C double bond in the ring.

Gas electron diffraction studies conducted by Yokezeki and Kuchitsui (1971) have shown all C–C–C bonds associated with norbornane to be appreciably smaller than the optimal tetrahedral angle; the bridging methylene C_1–C_7–C_4 angle is particularly acute at 93.1° ±1.7, while the cyclohexane C_1–C_2–C_3 angle is reported as 103.3° ±1.8. The combination of angular and torsional strain, together with C–C bond lengths greater than conventional distances due to the bridging group, contribute to the high-energy associated with the norbornane structure. The norbornene structure incorporates a double bond into the already strained norbornane system. The additional tension associated with norbornene structure is primarily attributed to angle strain. The unsaturated carbons are formally sp^2 hybridised, substituents of carbon–carbon double bonds are conventionally considered planar with a bond angle of 120°.

Holtausen and Koch (1993) conducted *ab initio* quantum chemical calculations on the structure of norbornene, and found the hydrogen bound to the unsaturated carbons to be bent in the *endo* (opposite side to methylene bridge) direction. The Holtausen and Koch paper reports an out of plane angle of 7.9° and a C_1–C_2–C_3 bond angle of 107.3°. There is greater divergence from model internal carbon bond angles with the norbornene structure than with norbornane, which when coupled with the torsional strain associated with the bicyclic system, result in considerable strain imparted on the norbornene structure. This explains the trend in molecular energies associated with the norbornane and norbornene structures, and ultimately the increased reactivity of norbornene. In forming the primary ozonide, the carbon at the norbornene double bond changes from formally sp^2 to sp^3 hybridisation, while retaining the torsional strain from the eclipsing interactions of neighbouring carbon–hydrogen bonds, the molecule is therefore afforded relative relief of angle strain. This relief of angle strain is the major contribution to the swift rate with which norbornene reacts with ozone.

The fact that cyclopentene reacts more quickly than the simple regression would suggest, is consistent with the work of Greene and Atkinson (1994), who showed that small cyclo-alkenes are strained and this strain is released upon ozonolysis which results in the disruption of the ring by cleaving the C=C double bond. For the larger ring system of cyclooctene the ring strain would be expected to be much lower and it is not clear why this compound reacts more rapidly than expected. Finally, dicyclopentadiene also reacts much more rapidly than would be expected; this can be rationalised from the structure of dicyclopentadiene which is a cyclopentene ring fused to a norbornene ring, the arguments above presented for these compounds therefore also apply (in combination) for this alkene.

The rate constant for the reaction of ozone with terpinolene can be further rationalised as a linear combination of the rate constants obtained for the oxidation of the double bond in methyl cyclohexene (analogous to the *endo* double bond of terpinolene) and *t*-butyl isopropylidene cyclohexane (analogous to the *exo* bond of terpinolene). From comparison of the rate constants it is apparent that ~19% of oxidation occurs at the *endo* double bond. At first glance this seems at odds with a previous study in this laboratory which estimated an upper limit of ~1% of the oxidation occurring at the *endo* double bond based on a study of the product yields of organic acids from terpinolene ozonolysis (Ma and Marston, 2009). The uncertainties in the measured rate constants are, however, large enough to encompass this observation as the fastest rate constant for terpinolene supported by our measurements (k + uncertainty) is faster than that obtained for *t*-butyl isopropylidene cyclohexane. It is well known that rationalising the kinetic behaviour of ozone–alkene reactions is somewhat more difficult than rationalising the kinetics of the reactions of OH or NO_3 radicals; see Johnson and Marston (2008) for example. Alternative approaches to the problem have been adopted. For example, McGillen et al. (2008) have developed a structure activity relationship that takes into account inductive and a detailed consideration of steric effects. This approach has been found to work well for a wide range of open chain alkenes and conjugated dienes.

3.4. NO_3 reactions

From Fig. 4 it is immediately apparent that all of the alkenes lie close to the regression line. The slower than expected rate of reaction of α-pinene and norbornene could be due to the steric effects of the bridgehead carbon out of the plane of the ring inhibiting the approach of the NO_3 radical to the double bond. While this bridgehead carbon is also present in dicyclopentadiene the effect will be mitigated by the availability of the second double bond in the structure which is contained in a cyclopentene moiety. It is worth noting that other approaches to rationalising the kinetics of NO_3 reactions have been developed. For example, Kerdouci et al. (2010) have recently reported a structure activity relationship based on that of Atkinson (1986) that successfully predicts rate coefficients for the reactions of NO_3 with some 150 unsaturated compounds with a wide range of substituents.

4. Atmospheric implications

From the rate constants obtained in this work atmospheric lifetimes with respect to oxidation by ozone or NO_3 can be calculated for each alkene from the following equation:

$$\tau_{\text{oxidant}} = \frac{1}{k[\text{oxidant}]}$$

Table 5
Calculated atmospheric lifetimes with respect to oxidation by ozone, NO_3 and OH radicals.

Compound	$\tau(O_3)$/h	$\tau(NO_3)$/h	τ(OH)/h
Methyl cyclohexene	2.45	0.14	3.26[a]
Terpinolene	0.26	0.02	1.42[a]
Ethylidene cyclohexane	1.45	0.26	–
Norbornene	0.34	4.21	4.61[a]
t-Butyl isopropylidene cyclohexane	0.21	–	–
Cyclopentene	0.59	1.61	4.86[b]
Cyclohexene	3.94	2.09	4.12[c]
Cyclooctene	0.71	2.19	–
Dicyclopentadiene	0.22	0.93	–
α-Pinene	3.38	0.22	5.21[c]

[a] Rate constants for calculation of OH lifetimes from Peeters et al. (2007).
[b] Rate constants for calculation of OH lifetimes from Rogers (1989).
[c] Rate constants for calculation of OH lifetimes from Atkinson (1986).

Assuming background concentrations of 35 ppbv (8.61×10^{11} molecule cm^{-3}) for ozone, a night time concentration of 10 pptv (2.46×10^8 molecule cm^{-3}) for NO_3 and a day-time concentration of 1×10^6 molecules cm^{-3} for OH (Finlayson-Pitts and Pitts, 2000) the lifetimes in Table 5 are obtained.

During the day these compounds will primarily be oxidised by ozone as despite its lower reactivity than with OH it is present in much higher concentrations. The calculated lifetimes with respect to reaction with ozone and NO_3 show that at night – when the OH concentration is close to zero – these compounds are oxidised with lifetimes between a few minutes and a few hours. Our data indicates that methyl cyclohexene, terpinolene, ethylidene cyclohexane and α-pinene are predominantly oxidised by the nitrate radical. Cyclohexene is oxidised almost equally by both O_3 and NO_3 and the remainder of the compounds for which data are available are predominantly oxidised by ozone.

5. Conclusions

A relative rate study has yielded room-temperature rate constants for the reactions of ozone and NO_3 with selected monoterpenes and cyclic alkenes. With the exception of norbornene the presented values are in agreement with literature values or are the first determination of these rate constants. A correlation is observed between the logarithm of the rate constant and the calculated HOMO energy for simple alkenes, the kinetic data from this study has been discussed with reference to this correlation is an attempt to rationalise the observed rate constants, deviations from the linear regression being attributed to moieties within the structure of the molecules.

Calculated atmospheric lifetimes suggest the studied reactions to be key night-time loss processes with NO_3-initiated oxidation dominating for the large majority of the investigated compounds during night time hours and oxidation by ozone predominating during the day.

References

Aird, R.W.S., Canosa-Mas, C.E., Cook, D.J., Marston, G., Monks, P.S., Wayne, R.P., 1992. Kinetics of the reactions of the nitrate radical with a series of halogenobutenes – a study of the effect of substituents on the rate of addition of NO_3 to alkenes. Journal of the Chemical Society – Faraday Transactions 88, 1093–1099.

Aschmann, S.M., Tuazon, E.C., Arey, J., Atkinson, R., 2011. Products of the OH radical-initiated reactions of 2-propyl nitrate, 3-methyl-2-butyl nitrate and 3-methyl-2-pentyl nitrate. Atmospheric Environment 45 (9), 1695–1701.

Atkinson, R., 1986. Kinetics and mechanism of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. Chemical Reviews 86, 69–201.

Atkinson, R., 1991. Kinetics and mechanisms of the gas-phase reactions of the NO_3 radical with organic compounds. Journal of Physical Chemistry Reference Data 20, 459–507.

Barnes, I., Bastian, V., Becker, K.H., Tong, Z., 1990. Kinetics and products of the reactions of NO_3 with monoalkenes, dialkenes and monoterpenes. Journal of Physical Chemistry 94, 2413–2419.

Berndt, T., Böge, O., 1997. Products and mechanism of the gas-phase reaction of NO_3 radicals with alpha pinene. Journal of the Chemical Society – Faraday Transactions 93, 3021–3027.

Charlson, R.J., Schwartz, S.E., Hales, J.M., Cess, R.D., Coakley Jr., J.A., Hansen, J.E., Hoffmann, D.J., 1992. Climate forcing by anthropogenic aerosols. Science 255, 423–430.

Clayden, J., Greeves, N., Warren, S., Wothers, P., 2001. Organic Chemistry. Oxford University Press, New York.

Cusick, R.D., Atkinson, R., 2005. Rate constants for the gas-phase reactions of ozone with a series of cycloalkenes at 296 +/– 2 K. International Journal of Chemical Kinetics 37, 183–190.

Donaldson, K., Li, X.Y., MacNee, W.J., 1998. Ultrafine (nanometre) particle mediated lung injury. Journal of Aerosol Science 29, 553–560.

Finlayson-Pitts, B.J., Pitts Jr., J.N., 2000. Chemistry of the Upper and Lower Atmosphere. Academic Press, San Diego.

Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery Jr., J.A., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., Pople, J.A., 2003. Gaussian, Inc., Pittsburgh PA.

Gaschen, A., Lang, D., Kalberer, M., Savi, M., Geiser, T., Gazdhar, A., Lehr, C.-M., Bur, M., Dommen, J., Baltensperger, U., Geiser, M., 2010. Cellular responses after exposure of lung cell cultures to secondary organic aerosol particles. Environmental Science & Technology 44 (4), 1424–1430.

Greene, C.R., Atkinson, R., 1992. Rate constants for the gas-phase reactions of ozone with a series of cycloalkenes at 296 +/– 2 K. International Journal of Chemical Kinetics 24, 803–811.

Greene, C.R., Atkinson, R., 1994. Rate constants for the gas-phase reactions of ozone with a series of cycloalkenes and alpha, beta unsaturated ketones at 296 +/– 2 K. International Journal of Chemical Kinetics 26, 37–44.

Grosjean, E., Grosjean, D., 1995. Rate constants for the gas-phase reactions of C5-C10 alkenes with ozone. International Journal of Chemical Kinetics 27, 1045–1054.

Harrison, J.C., Ham, J.E., 2009. Beta-ionone reactions with the nitrate radical: rate constant and gas phase products. International Journal of Chemical Kinetics 41, 629–641.

Holtausen, M.C., Koch, W., 1993. Double-bond geometry in norbornane, sesquinorbornenes, and related compounds – a high level quantum chemical investigation. Journal of Physical Chemistry 97, 10021–10027.

Johnson, D., Marston, G., 2008. The gas-phase ozonolysis of unsaturated volatile organic compounds in the troposphere. Chemical Society Reviews 37, 699–716.

Johnson, D., Rickard, A.R., McGill, C.D., Marston, G., 2000. The influence of orbital asymmetry on the kinetics of the gas-phase reactions of ozone with unsaturated compounds. Physical Chemistry Chemical Physics 2, 323–328.

Kerdouci, J., Picquet-Varrault, B., Doussin, J.-F., 2010. Prediction of rate constants for gas-phase reactions of nitrate radical with organic compounds: a new structure-activity relationship. ChemPhysChem 11, 3909–3920.

Kind, I., Berndt, T., Böge, O., 1998. Gas-phase rate constants for the reaction of NO_3 radicals with a series of cyclic alkenes, 2-ethyl-1-butene and 2,3-dimethyl-1,3-butadiene. Chemical Physics Letters 288, 111–118.

King, M.D., Canosa-Mas, C.E., Wayne, R.P., 1999. Frontier molecular orbital correlations for predicting rate constants between alkenes and tropospheric oxidants, NO_3, OH and O_3. Physical Chemistry Chemical Physics 1, 2231–2238.

Ljungstrom, E., Wangberg, I., Langer, S., 1993. Absolute rate coefficients for the reaction between nitrate radicals and some cyclic alkenes. Journal of the Chemical Society – Faraday Transactions 89, 2977–2982.

Ma, Y., Marston, G., 2009. Formation of organic acids in the gas-phase ozonolysis of terpinolene. Physical Chemistry Chemical Physics 11, 4198–4209.

Marti, J.J., Weber, R.J., McMurry, P.H., Eisele, F., Tanner, D., Jefferson, A., 1997. New particle formation at a remote continental site: assessing the contributions of SO_2 and organic precursors. Journal of Geophysical Research – Atmospheres 102 (D5), 6331–6339.

Martinez, E., Cabanas, B., Aranda, A., Martin, P., Salgado, S., 1999a. Absolute rate coefficients for the gas-phase reactions of NO_3 radical with a series of monoterpenes at T = 298 – 433K. Journal of Atmospheric Chemistry 33, 265–282.

Martinez, E., Cabanas, B., Aranda, A., Martin, P., Salgado, S., 1999b. Study on the NO_3 radical reactivity: reactions with cyclic alkenes. Journal of Physical Chemistry A 103, 5321–5327.

McGillen, M.R., Carey, T.J., Archibald Wenger, J.C., Shallcross, D.E., Percival, C.J., 2008. Structure-activity relationship (SAR) for the gas-phase ozonolysis of aliphatic alkenes and dialkenes. Physical Chemistry Chemical Physics 10, 1757–1768.

Nolting, F., Behnke, W., Zetzsch, C., 1988. A smog chamber for the studies of the reactions of terpenes and alkanes with ozone and OH. Journal of Atmospheric Chemistry 6, 47–59.

Novakov, T., Penner, J.E., 1993. Large contribution of organic aerosols to CCN concentrations. Nature 365, 823–826.
Osborne, B.A., Marston, G., Kaminski, L., Jones, N.C., Gingell, J.M., Mason, N., Walker, I.C., Delwiche, J., Hubin-Franksin, M.J., 2000. Vacuum ultraviolet spectrum of dinitrogen pentoxide. Journal of Quantitative Spectroscopy and Radiative Transfer 64, 67–74.
Paulson, S.E., Orlando, J.J., 1996. The reaction of ozone with alkenes: an important source of HO_x ion the boundary layer. Geophysical Research Letters 23, 3727–3730.
Peeters, J., Boullart, W., Pultau, V., Vandenberk, S., Vereecken, L., 2007. Structure activity relationship for the addition of OH to (poly)alkenes: site-specific and total rate constants. Journal of Physical Chemistry A 111, 1618–1631.
Perraud, V., Bruns, E.A., Ezell, M.J., Johnson, S.N., Greaves, J., Finlayson-Pitts, B.J., 2010. Identification of organic nitrates in the NO_3 radical initiated oxidation of alpha-pinene by atmospheric pressure chemical ionisation mass spectrometry. Environmental Science & Technology 44, 5887–5893.
Pfrang, C., Martin, R.S., Nalty, A., Waring, R., Canosa-Mas, C.E., Wayne, R.P., 2005. Gas-phase rate coefficients for the reactions of nitrate radicals with (Z)-pent-2-ene, (E)-pent-2-ene, (Z)-hex-2-ene, (E)-hex-2-ene, (Z)-hex-3-ene, (E)-hex-3-ene, (E)-3-methylpent-2-ene at room temperature. Physical Chemistry Chemical Physics 7, 2506–2512.
Pfrang, C., King, M.D., Canosa-Mas, C.E., Wayne, R.P., 2006a. Structure-activity relationships for gas-phase reactions of NO_3, OH and O_3 with alkenes: an update. Atmospheric Environment 40, 1180–1186.
Pfrang, C., King, M.D., Canosa-Mas, C.E., Wayne, R.P., 2006b. Correlations for gas-phase reactions of NO_3, OH and O_3 with alkenes: an update. Atmospheric Environment 40, 1170–1179.
Pfrang, C., King, M.D., Canosa-Mas, C.E., Flugge, M., Wayne, R.P., 2007. Gas-phase rate coefficients for the reactions of NO_3, OH and O_3 with alpha, beta unsaturated esters and ketones: structure-activity relationships. Atmospheric Environment 41, 1792–1802.
Pfrang, C., King, M.D., Braeckevelt, M., Canosa-Mas, C.E., Wayne, R.P., 2008. Gas-phase rate coefficients for reactions of NO_3, OH, O_3 and O(3P) with unsaturated alcohols and ethers: correlations and structure-activity relationships. Atmospheric Environment 42, 3018–3034.
Rogers, J.D., 1989. Rate constant measurements for the reaction of the hydroxyl radical with cyclohexene, cyclopentene and glutaraldehyde. Environmental Science & Technology 23, 177–181.
Shu, Y., Atkinson, R., 1994. Rate constants for the gas-phase reactions of O_3 with a series of terpenes and OH radical formation from the O_3 reaction with sesquiterpenes at 296 +/− 2 K. International Journal of Chemical Kinetics 26, 1193–1205.
Suarez-Bertoa, R., Picquet-Varrault, B., Tamas, W., Pangui, E., Donssin, J.-F., 2012. Atmospheric fate of carbonyl nitrates: photolysis frequencies and OH-oxidation rate constants. Environmental Science & Technology 46 (22), 12502–12509.
Treacy, J., Curley, M., Wenger, J., Sidebottom, H., 1997. Determination of Arrhenius parameters for the reactions of ozone with cycloalkenes. Journal of the Chemical Society – Faraday Transactions 93, 2877–2881.
Twomey, S.A., Piepgrass, M., Wolfe, T.L., 1984. An assessment on the impact of pollution on global cloud albedo. Tellus – Series B. Chemical and Physical Meteorology 36B, 356–366.
Went, F.W., 1960. Blue hazes in the atmosphere. Nature 187, 641–643.
Witter, M., Berndt, T., Böge, O., Stratmann, F., Heintzenberg, J., 2002. Gas-phase ozonolysis: rate coefficients for a series of terpenes and rate coefficients and OH yields for 2-methyl-2-butene and 2,3-dimethyl-2-butene. International Journal of Chemical Kinetics 34, 394–403.
Yokezeki, A., Kuchitsui, K., 1971. Structures of norbornane and norbornadiene as determined by gas electron diffraction. Bulletin of the Chemical Society of Japan 44, 2356–2363.